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supplementary information

A new diphosphine-carbonyl complex of ruthenium: An efficient precursor for C-C and C-N coupling catalysis†

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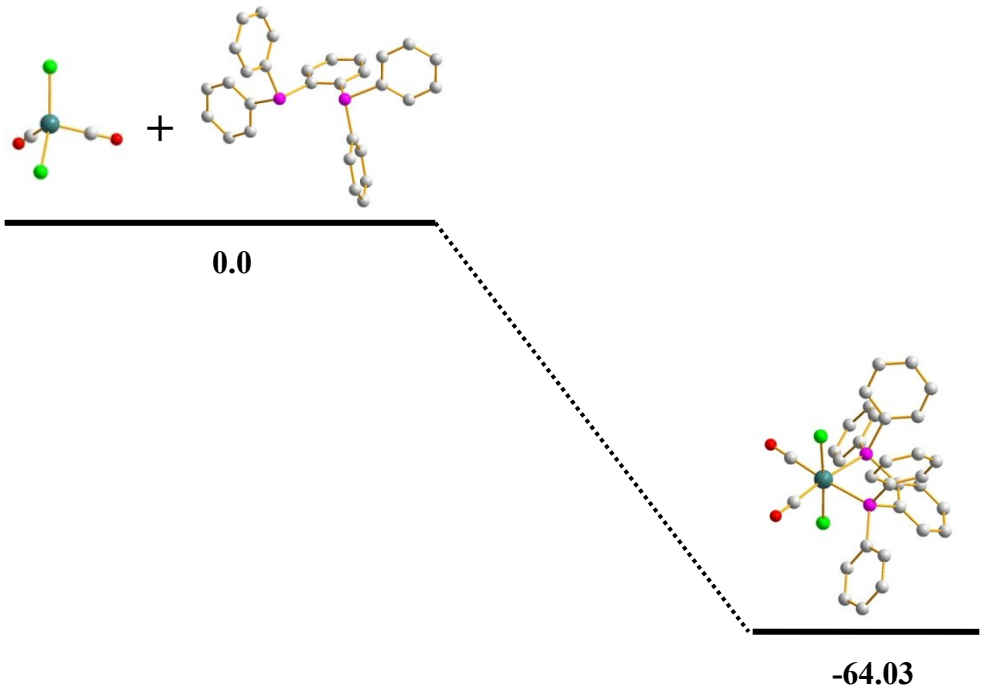


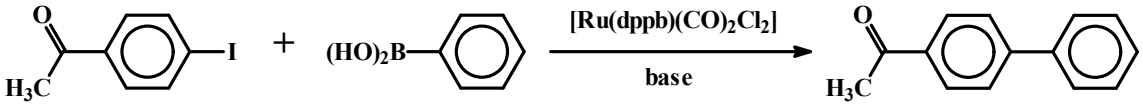
Fig. S1 DFT-optimized structures and ground-state energy ordering for the reaction of $Ru(CO)_2Cl_2$ (**A**) and 1,2-bis(diphenylphosphino)benzene (**B**) to give the complex $[Ru(dppb)(CO)_2Cl_2]$ (**C**). The free energy values (in kcal/mol) are referenced relative to the reagents (**A**+**B**).

Table S1

Selected bond lengths (Å) and bond angels (°) for the X-ray diffraction structure of $[Ru(dppbz)(CO)_2Cl_2]$

Bond lengths (Å)			
Ru1-Cl1	2.4178(6)	C7-O1	1.125(3)
Ru1- Cl2	2.3958(6)	C8-O2	1.130(3)
Ru1-P1	2.3833(6)	P1-C1	1.827(2)
Ru1-P2	2.4034(7)	C1-C6	1.395(3)
Ru1-C7	1.926(2)	P2-C6	1.832(2)
Ru1-C8	1.910(3)		
Bond angles (°)			
Cl1-Ru1-Cl2	177.80(2)	P1-Ru1-P2	80.83(2)
P1-Ru1-C7	172.38(7)	Ru1-C7-O1	175.5(2)
P2-Ru1-C8	171.24(7)	Ru1-C8-O2	174.8(2)

Table S2 Suzuki cross coupling of aryl iodides with phenylboronicacid[a]

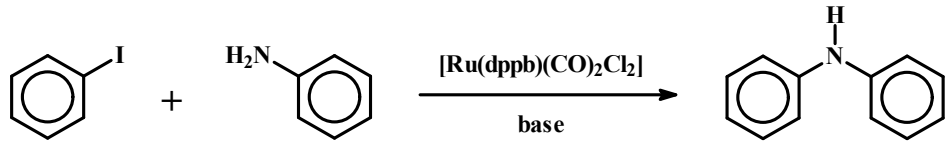


Entry	Solvent	Mole % of catalyst	Base	Amount of base (mmol)	Temperature, ºC	Time, h	Yield[b], %
1	toluene	1	NEt_3	1	140	24	NO
2	toluene	1	K_3PO_4	1	140	24	62
3	toluene	1	K_3PO_4	1.5	140	24	68
4	toluene	1	KO^tBu	1	140	24	41
5	toluene	1	KO^tBu	1.5	140	24	43
6	toluene + ethanol	1	K_3PO_4	1.5	140	24	53
7	PEG	1	K_3PO_4	1	140	24	87
8	PEG	1	K_3PO_4	1.5	140	24	96
9	PEG	0.5	K_3PO_4	1.5	140	24	40
10	PEG	1	K_3PO_4	1.5	120	24	66
11	PEG	1	K_3PO_4	1.5	140	32	97
12	PEG	1	K_3PO_4	1.5	140	18	76

[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), solvent (5 mL).

[b] Determined by GCMS.

Table S3 C-N cross-coupling reaction of aryl halides with amines[a]



Entry	Solvent	Mole % of catalyst	Base	Amount of base (mmol)	Temperature, ºC	Time, h	Yield [b], %
1	PEG	2	N_2H_4	1.0	130	24	76
2	PEG	2	N_2H_4	1.0	130	36	79
3	PEG	2	N_2H_4	1.0	130	18	57
4	PEG	1	N_2H_4	1.0	130	24	41
5	PEG	1	K_3PO_4	1.5	140	24	28
6	PEG	1	NaO^tBu	1.5	140	24	NO
7	toluene	1	K_3PO_4	1.0	100	24	16
8	toluene	1.5	K_3PO_4	1.0	100	24	12
9	toluene	2.0	N_2H_4	1.5	100	24	13
10	toluene + ethanol	1	K_3PO_4	1.0	100	24	21
11	toluene + ethanol	1.5	K_3PO_4	1.0	100	24	24
12	toluene + ethanol	2.0	N_2H_4	1.5	100	24	17

[a] Reaction conditions: aryl halide (1.0 mmol), amines (1.2 mmol), solvent (5 mL).

[b] Determined by GCMS.

Table S4 X-ray diffraction and processing parameters for $[Ru(dppb)(CO)_2Cl_2]$

empirical formula	$C_{32}H_{24}Cl_2O_2P_2Ru$, $1[CH_2Cl_2]$
formula weight	759.35
crystal system	Triclinic
space group	$P\bar{1}$
a (Å)	9.0132(2)
b (Å)	11.0476(3)
c (Å)	18.2117(5)
α (◦)	75.668(1)
β (◦)	76.977(1)
γ (◦)	68.398(1)
V (Å^3)	1615.34(7)
Z	2
F (000)	680
crystal size (mm)	0.08 × 0.12 × 0.35
T (K)	273
μ (mm^{-1})	0.945
R1[a]	0.0252
wR2[b]	0.0593
GOF[c]	1.05

[a] $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

[b] $wR2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)\}]^{1/2}$.

[c] $GOF = [\Sigma(w(F_o^2-F_c^2)^2)/(M-N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

Table S5 Cartesian coordinates for all molecules in Figures 9 and 10 with computed electronic and zero-point energies (attached separately; **19 pages**).